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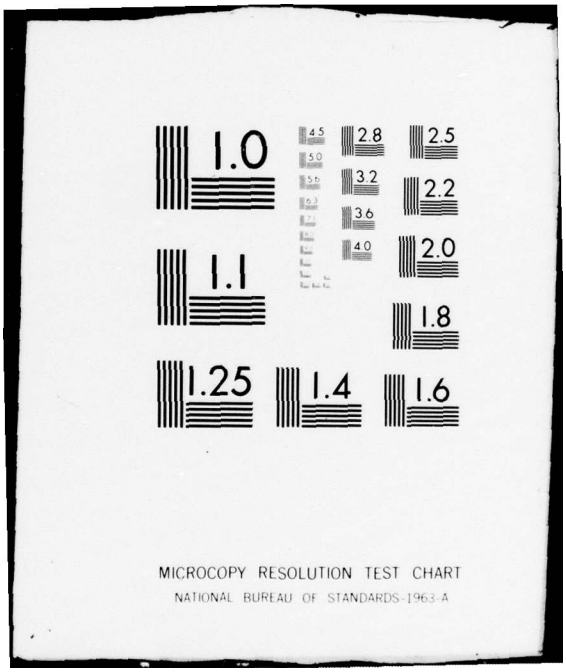
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The mechanical model of Takayanagi has been used to describe the viscoelastic behavior of various blends of a ternary elastomer system (cis 1,4 polyisoprene, 1,4 polybutadiene and the corresponding polyisoprene/polybutadiene diblock) for which extensive mechanical properties data have already been reported. Through the use of appropriate composition - temperature shifts which rely on the assumption of free volume additivity, it was possible to model the behavior of the homogeneous diblock copolymers of polyisoprene and polybutadiene as well as various homogeneous binary and ternary blends of a diblock with either or both

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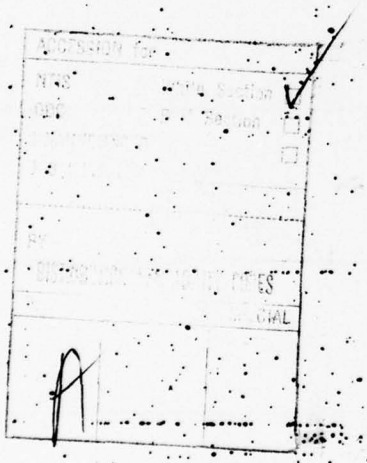
of the diene homopolymers. Heterogeneous ternary blends were also modelled successfully assuming that the diblock was solubilized preferentially by one of the phases in the blend. The model predictions were very sensitive to the location of the diblock, and thus comparison with experimental results provided a useful tool for verifying earlier assumptions regarding the role of the homogeneous diblock copolymers in these elastomer blends.



MODELLING OF THE VISCOELASTIC BEHAVIOR OF HOMOGENEOUS AND HETEROGENEOUS BLENDS OF POLYISOPRENE AND POLYBUTADIENE

by

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INTRODUCTION

The viscoelastic behavior of a multicomponent polymer depends upon the properties of the individual components and the manner in which these properties are 'coupled' to yield the overall material response. One manifestation of this coupling of viscoelastic mechanisms is the well-documented 'thermorheologically complex' behavior of heterogeneous block copolymers and heterogeneous polymer blends (1); such behavior is particularly evident in data obtained in a series of isothermal viscoelastic experiments conducted over a range of time or frequency. A single isochronal experiment, conducted at a fixed time or frequency over a range of temperatures, is more commonly reported in the literature on multicomponent polymers, and it is for the purpose of describing such data that numerous 'mechanical models' have been proposed and tested (2-4).

Among these, the Takayanagi model (2) has enjoyed the most widespread use, owing to its relative simplicity and its flexibility in fitting a wide range of data. Originally, Takayanagi proposed that there were two variants of his model with one variant being more suitable for the bulk of experimental data examined; more recently Tschoegl and coworkers (5) pointed out that the two variants are entirely equivalent and that the parameters of one variant are uniquely related to the parameters of the other. In both cases the Takayanagi model proposes that two distinct phases are coupled and that this coupling is partly series and partly parallel.

In the present paper we are interested in using the Takayanagi model to describe the behavior of various homogeneous and heterogeneous blends of polybutadiene and polyisoprene for which we have obtained extensive viscoelastic data (6-9). Although more complicated models could be used, our purpose here is not to find the optimal model which gives the best curve fits to the data. Instead we will use the relatively simple Takayanagi model to seek physical insights into the nature of the viscoelastic response of our materials. In particular the presence of both homogeneous and heterogeneous blends in the array of specimens examined will lead to some insight regarding the relative importance of parallel and series coupling in these two cases. Furthermore, the degree of fit of an appropriately constituted Takayanagi model may be used to verify certain postulates made earlier (6,8,10) regarding the mutual solubility of various components of the ternary system studied. Finally, the modelling in this study will add support to the earlier conclusion (7) that these particular diblock samples are essentially homogeneous materials. Taken overall, the results presented below indicate that appropriate modelling studies can be used as an independent tool for obtaining important information on the phase structures and their interactions in both homogeneous and heterogeneous multicomponent polymer systems.

MATERIALS AND METHODS

The homopolymers employed in the experimental program were cis 1,4 polyisoprene and medium cis 1,4 polybutadiene. Three polybutadiene/

polyisoprene diblock copolymers were provided by Dr. Paul Rempp of the Centre of Rechercher sur les Macromolecules, Strasbourg, France. These copolymers were synthesized under appropriate conditions to match the individual block microstructures with the selected homopolymers. Detailed characterization information for all polymers has appeared in previous publications (6,7).

Blends of various composition were prepared by solvent casting techniques according to procedures described elsewhere (6,10). A variety of experimental characterization methods were applied to these blends, including thermal analysis, transmission electron microscopy and dynamic mechanical testing. In the latter set of experiments a Rheovibron viscoelastometer was used at four different frequencies in the range 3.5 Hz to 110 Hz and at temperatures from -135° C to 40° C. Appropriate gripping methods (11) were employed to minimize the importance of the correction factors (9) which are required when soft polymers are studied in the tensile geometry on the Rheovibron.

The results of the overall experimental program are summarized schematically in Figure 1. Each triangle represents a ternary composition diagram for the components: polybutadiene/polyisoprene diblock copolymer (COP), polybutadiene homopolymer (BR), and polyisoprene homopolymer (IR). The three copolymers differed in the relative lengths of the constituent block segments; values of 2/1, 1/1 and 1/2 were employed for the molar ratio of repeat units of butadiene and isoprene in the three diblocks. As shown by the shaded regions in Figure 1, homogeneous systems were obtained in various regions of the three ternary composition diagrams.

THE TAKAYANAGI MODEL

In the Takayanagi model, two interdependent parameters λ and ϕ are used to describe the coupling of the properties of the components of composite systems. The value of the product $\lambda\phi$ is set equal to the volume fraction of the minor component, usually also taken to be the discontinuous phase of a two-phase composite. As can be seen from the schematic representation of the Takayanagi model in Figure 2, the coupling approaches that of a simple series model as $\lambda \rightarrow 1$, and simple parallel coupling is approached as $\phi \rightarrow 1$.

The Takayanagi model thus leads to expressions for the viscoelastic properties of a two component system of the following form

$$E(t,T) = [1-\lambda]\, E_A(t,T) + \lambda \left\{ \frac{[1-\phi]}{E_A(t,T)} + \frac{\phi}{E_B(t,T)} \right\}^{-1} \qquad (1)$$

where $E(t,T)$ is the time and temperature dependent relaxation modulus for the composite, expressed in terms of the moduli of the major component A and the minor component B. Because $\lambda\phi = v_B$ = the volume fraction of the minor component, Equation (1) reduces to

$$E(t,T)_{\lambda=1} = \left\{ \frac{1-v_B}{E_A(t,T)} + \frac{v_B}{E_B(t,T)} \right\}^{-1} \qquad (2)$$

for series coupling and to

$$E(t,T)_{\phi=1} = (1-v_B)\, E_A(t,T) + v_B\, E_B(t,T) \qquad (3)$$

for parallel coupling.

Because we will be concerned with modelling of dynamic mechanical data, the complex modulus $E^*(\omega,T)$ will replace the relaxation modulus in Equations 1-3. As shown in the Appendix it is then a matter of straightforward algebraic rearrangement to obtain epxressions for the storage modulus E' and the loss modulus E" and their ratio, the loss tangent, E"/E'.

In the present paper we will be content with the simple case in which λ and ϕ are independent of time or frequency and temperature; Variations of λ and ϕ with time and temperature (the product $\lambda\phi$ remaining constant) have been introduced (5) in order to obtain acceptable fit of the Takayanagi model to certain sets of data, with the proposed justification that the coupling may indeed vary with both time and temperature. Other modifications have also been proposed to eliminate (3) the anisotropy in the Takayanagi model which always exists when $\lambda \neq \phi$ and to improve (4) the fitting ability of the model near $\lambda\phi = 0.5$ when co-continuous phases may exist. We shall not make use of either of these modifications because they offer little extra physical insight in the interpretation of our particular set of viscoelastic data.

APPLICATION OF THE MODEL TO POLYISOPRENE-POLYBUTADIENE BLENDS

Our earlier experimental results revealed several cases in which homogeneous binary blends were obtained; also, there were numerous instances in which ternary mixtures of the two homopolymers and a block copolymer formed heterogeneous systems in which either one or both of the two phases present were of mixed composition (i.e. neither pure

IR or BR). For these reasons, we will present our modelling results in stages, beginning with the description of the behavior of a homogeneous blend (or phase) of mixed composition and moving toward the general case of a two-phase heterogeneous blend in which each phase may be of intermediate composition between pure IR and pure BR. If successful, the latter model will allow us to describe the behavior of our ternary systems (IR, BR and IR/BR diblocks) in terms of the properties of only two of the components (IR and BR). This rather unusual situation is made possible by the fact that the diblock copolymers used in this study were essentially homogeneous materials (7) and in various cases could be solubilized by one or both of the homopolymers (6,8,9).

Modelling of Homogeneous Blends and Diblocks

As the first step in the development, modelling of the diblocks and of homogeneous blends of a diblock and one of the homopolymers will be undertaken. A basic assumption at this point is the additivity of free volumes. The fraction of free volume in a homogeneous mixture of IR and BR segments is assumed to be equal to the arithmetic mean value of the free volume fractions of IR and BR, all taken at the same temperature. This assumption may be justified in the present case by the previously obtained experimental evidence that the Gordon-Taylor equation (12) could be used successfully to describe the composition dependence of the glass transition temperatures of the three diblocks. A second assumption is that the relaxation times of the various materials can be expressed in terms of the free volume only. That is, the pure

temperature contribution to the relaxation times is considered to be negligible in the present case; for other systems, such as polyvinyl acetate, this contribution has been found to amount to about 20% of the total (*13*).

At any temperature above the BR glass transition, the fractional free volume in pure polybutadiene, f_B is larger than that in pure polyisoprene, f_I (*14*). Therefore, in a blend of the two homopolymers the polybutadiene molecules would be in an environment of reduced free volume compared to pure polybutadiene at the same temperature. The polyisoprene molecules in a homogeneous blend, would be in the opposite situation. This effect is equivalent to that observed in the plasticization of polymers by low molecular weight diluents. In the present case, polybutadiene effectively acts as a plasticizer for polyisoprene.

The free volume fraction is a function of temperature. Thus, a polybutadiene chain in a homogeneous blend with polyisoprene at a temperature T_c will experience a free volume environment equivalent to that it would have had in pure polybutadiene at a lower temperature T_B. A polyisoprene molecule in the same blend is in a free volume environment that would exist in pure polyisoprene at a temperature T_I which is greater than T_C. If, according to the assumptions stated above, the time-scales of mechanical relaxation can be expressed in terms of the free volume only, then the contribution of each component to the overall properties of a <u>homogeneous</u> blend should be related to the pure component properties taken at a condition of equivalent free volume. (For a <u>heterogeneous</u> blend the constituent contributions are all taken at a

common temperature). In the present case, the properties of the homogeneous blend at T_C will be modelled by combining the properties of polyisoprene determined at temperature T_I and those of polybutadiene at T_B. Expressions for T_I and T_B are presented in the Appendix. Both T_I and T_B will depend upon: blend composition; Tc; fractional free volume of each component at its respective T_g, f_{gI} and f_{gB}; and the thermal expansion of free volume relative to total volume for each component, α_{fI} and α_{fB}.

Published values (*14*) of T_g and α_f for IR and BR were used; these are shown in Table 1. Model predictions using the reported values (*14*) of f_{gI} and f_{gB} did not produce satisfactory results. Instead f_{gI} and f_{gB} were taken to be equal to each other in which case their absolute values had no effect on the model predictions. The assignment of the same value to f_{gI} and f_{gB} is not without precedent. Fox and Flory (*15*) first introduced to the view that the free volume at the glass transition temperature should be a constant for all polymers. In fact, for the great majority of systems $f_g = 0.035 \pm 0.005$ (*14*). We also note that because α_{fB} is larger than α_{fI}, the difference $T_I - T_B$ increases with T_c, the temperature at which the blend is being modelled. On the other hand, the dimensionless ratio $(T_c - T_B)/(T_I - T_B)$ is independent of temperature and depends only on composition (*10*).

In Figure 3, the appropriate modelling temperatures are illustrated for the case of a polybutadiene/polyisoprene diblock with segments of equal number of repeat units - COP 2143 (1/1). In this figure T_I and T_B are plotted vs. T_c. Note that both T_I and T_B are linear functions of T_c and that they diverge. The lower set of horizontal dashed lines

in the figure represent the glass transition temperatures of IR and BR. Intersection points 1 and 3 fall on a vertical line, the simple geometry resulting from the assumption that the free volume fraction at T_g is equal for both homopolymers. According to Figure 2, the glass transition of the diblock 2143 (1/1) predicted to be is 186° K(-87° C). The values determined experimentally by thermomechanical analysis (7,10) at a heating rate of 5° C/minute was -80° C.

The upper set of three horizontal broken lines in the Figure 3 represents the location of the loss tangent peaks at 3.5 Hz for the two homopolymers and diblock 2143 (1/1). They are indicated as T_g (3.5 Hz). Note again that intersection of points 4 and 6 fall on a vertical line, corresponding to a T_c of 208° K (-65° C). This is a

further indication of the consistency of the model with experimental data since the value of T_c = -65° C is identical to the experimentally determined location of COP 2143 (1/1) loss peak (point 5). Similar figures constructed for the two other diblocks also showed agreement with experiment to within 2° K. The significance of this consistency is that in modelling the properties of a homogeneous blend or block copolymer, one must use the properties of the constituents as measured in experiments of similar characteristic time-scales (i.e. heating rate, frequency, etc.).

Expressions for T_I and T_B were used to determine the contribution of each component in a homogeneous blend to the complex modulus, E*, at a temperature, T_c, and frequency ω. Referring to the Appendix, the polyisoprene contribution is:

$$v_I \frac{T_c}{T_I} E_I^* (T_I, \omega) \tag{4}$$

and the polybutadiene contribution:

$$v_B \frac{T_c}{T_B} E_B^* (T_B, \omega) \tag{5}$$

where E_I^* and E_B^* are the tensile complex moduli of polyisoprene and polybutadiene at the temperature and frequency indicated in parenthesis. The factors T_c/T_I and T_c/T_B are included as a consequence of the entropy contribution to rubber elasticity (*14*). Factors v_I and v_B take into account the decrease in the number density of polyisoprene and

polybutadiene molecules due to the dilution that takes place upon mixing.

In a homogeneous diblock, the chemical bond between the isoprene and butadiene segments acts as a perturbation that may influence the viscoelastic retardation times of both segments. Shen [16-18] has extended a bead-and-spring model to take into account this effect and computed retardation spectra for homogeneous block copolymers of styrene and α-methyl-styrene. In the present case, however, we have ignored any effect of this linkage bond on the physical properties of the diblock. In other words, we have assumed that there is no difference between a homogeneous diblock and an equivalent hypothetical homogeneous blend of IR and BR. This assumption is justified later by the degree of success of the model in predicting E' and tan δ curves for the diblocks and several homogeneous binary blends of a diblock and a homopolymer. In terms of the Takayanagi model, the complex modulus for the homogeneous blend is given by

$$E^*(T_c,\omega) = (1-\lambda)\frac{T_c}{T_k} E_k^* + \lambda\left[\frac{T_k(1-\phi)}{T_c E_k^*} + \frac{T_L\phi}{T_c E_L^*}\right]^{-1} \tag{6}$$

where

$$E_K^* = E_I^*(T_I,\omega) \tag{7}$$

$$E_L^* = E_B^*(T_B,\omega) \tag{8}$$

and $$\lambda\phi = v_B,\ T_k = T_I,\ T_L = T_B \tag{9}$$

if polyisoprene assumes the role of "continuous phase"; otherwise:

$$E_K^* = E_B^* (T_B, \omega) \tag{10}$$

$$E_L^* = E_I^* (T_I, \omega) \tag{11}$$

$$\lambda\phi = v_I, \; T_k = T_B, \; T_L = T_I \tag{12}$$

Note that E_K^* and E_L^* are not evaluated at the blend temperature T_c, but at the temperatures T_I and T_B. When either $\phi = 1$ (parallel coupling) or $\lambda = 1$ (series coupling) the model predictions are the same regardless of which materials is assumed to take the role of "continuous phase".

The effect of the type of coupling on the model predictions is illustrated in Figure 4 for diblock 2143 (1/1). The position of the loss peak is not affected by the type of coupling; properties in the rubbery region, however, are greatly affected. Comparison of the model predictions with experimental data indicates that simple parallel coupling provides an adequate fit to the data. The same conclusion was obtained in modelling COP 2144 (2/1) and COP 2148 (1/2). The success of this simple model in fitting the diblock curves provides some verification of our earlier assessment of these diblocks as essentiall homogeneous materials.

Homogeneous binary blends of one homopolymer and a diblock (see Figure 1) were treated in a similar fashion. Polybutadiene and poly-

isoprene fractions were calculated by taking into account isoprene and butadiene units present in the diblock itself and in the homopolymer. Model predictions for a 50:50 blend of COP 2143 (1/1) and IR are compared against experimental data in Figure 5. As with the diblocks, the model using parallel coupling closely followed the experimental curves.

All homogeneous binary blends considered in this study (COP 2144 (2/1) with BR, COP 2143 (1/1) with BR, COP 2143 (1/1) with IR, and COP 2148 (1/2) with IR, see Figure 1) were best represented in every case by the fully parallel Takayanagi model. In a few cases, particularly for blends containing COP 2144 (2/1) none of the different series-parallel couplings matched closely the experimental values; however, the purely parallel model was consistently better.

Modelling of Heterogeneous Homopolymer Blends

As mentioned in the Introduction, the Takayanagi model has been extensively applied to heterogeneous blends. In the previous section, the Takayanagi model was modified to take into account composition changes by applying suitable temperature shifts to the components' properties. Such modification is not necessary in modelling heterogenous blends of IR and BR homopolymers since each phase remains pure.

For a heterogeneous blend, the Takayanagi model is represented by

$$E^*(T_c,\omega) = (1-\lambda)E_M^* + \lambda \left[\frac{1-\phi}{E_M^*} + \frac{\phi}{E_N^*}\right]^{-1} \qquad (13)$$

where

$$E_M^* = E_I^* (T_c, \omega) \tag{14}$$

$$E_N^* = E_B^* (T_c, \omega) \tag{15}$$

$$\lambda\phi = v_B \tag{16}$$

if polyisoprene forms the continuous phase; otherwise

$$E_M^* = E_B^* (T_c, \omega) \tag{17}$$

$$E_N^* = E_I^* (T_c, \omega) \tag{18}$$

$$\lambda\phi = v_I \tag{19}$$

For convenience, it is useful to define a parameter to express the "degree of parallel" coupling of the model:

$$\% \text{ parallel} = \frac{\lambda(1-\phi)}{1-\phi\lambda} \times 100 \tag{20}$$

Thus for $\phi = 1$ (series coupling) % parallel = 0 and for $\lambda = 1$ (parallel coupling) % parallel = 100.

The effect of changing the degree of series-parallel coupling is illustrated in Figure 6. There, E' and tan δ are predicted for a 50/50

blend of BR and IR in which the polybutadiene phase is continuous (6,10). For 0% parallel (series coupling), the drop in modulus at the BR transition is very pronounced and a large loss peak is observed. At the IR transition, however, the drop in modulus is only moderate while a relatively small and broad loss peak is observed. On the other hand, for 100% parallel coupling, the drop in modulus and the corresponding loss peak at the BR transition are small, while both are large at the IR transition. In the rubbery region, the levels of modulus and tan δ approach those of IR (lower modulus and higher tan δ) as the model approaches a purely series coupling. In the glassy region, where the losses (i.e., tan δ) are very small, the degree of series-parallel coupling has little effect on the predicted properties. Experimental data obtained for this 50/50 blend of the two homopolymers are shown as the filled circles in Figure 5. The data points, both for E' and tan δ, are relatively closely fitted by a 75% parallel model. We also note that for the two extreme cases, i.e. 0% and 100% parallel, the model predicitons are independent of the choice of the phase taken to be continuous. The shapes of the E' and tan δ curves for intermediate degrees of series-parallel coupling are, in contrast, highly dependent on the choice for the continuous phase.

Figure 7 presents the model predictions for a 25/75 blend of BR and IR for which IR formed the continuous phase. The 0% and 100% parallel curves are similar in shape to those presented in Figure 6. For the intermediate curves, however, a large difference is observed. When BR is assumed to be continuous, as in the case of Figure 6, little

change in the shape of the curves in the transition region takes place in going from 0% to 50% parallel and the changes are increasingly rapid as the 100% parallel limit is approached. On the other hand, when IR is assumed to be continuous, as in Figure 7, most of the change in the behavior in the transition region is observed between 0 and 25% parallel. In the rubbery region the effects are opposite. That is, when BR is continuous the changes in the modulus and tan δ levels are smaller as 100% parallel is approached; when IR is continuous the changes in the levels of these two properties are larger as 100% parallel behavior is approached.

The corresponding experimental data for the 25/75 blend of BR and IR are also included in Figure 7. The shape of the E' and tan δ curves between the IR and BR transitions is matched by a model close to 100% parallel. In the rubbery region, however, the experiemntal points seem to follow the behavior of a 90% parallel coupling. This example illustrates clearly the advantage of comparing model and data in both the transition and the rubbery regions. While in the transition region the model indicates only that the coupling is close to 100% parallel, it is hard to be more precise because in this region the curves change little for models with coupling above 25% parallel. By considering the rubbery region simultaneously, however, it is possible to establish the degree of series-parallel to within a narrower range, since in this region the largest changes take place close to the 100% parallel behavior.

A summary of the results of modelling heterogeneous homopolymer

blends is presented in Table 2. The results indicate that as the amount of IR in the blend is increased, the behavior of the blend approaches 100% parallel.

Modelling of Heterogeneous Blends Containing a Homogeneous Diblock Copolymer

One of the main conclusions of our earlier papers (6,8) was that in ternary blends, the diblock copolymer is solubilized preferentially by the phase that is identical with the longer segment in the diblock (in the case of COP 2144 (2/1) and COP 2148 (1/2)) or by the continuous phase (in the case of COP 2143 (1/1)). As a consequence, the modelling of a blend containing a homogeneous diblock copolymer is carried out as follows. The composition of each pahse is determined under the assumption that the location of the diblock is known. Then, using Equations (6) to (12), the properties of each phase are determined, which are in turn used to calculate the overall modulus using Equation (13).

The procedure outlined above involves adjustable parameters at two levels. First, it is necessary to assign a value to the series-parallel character within each phase and then to the overall blend. There would be thus at least three adjustable parameters. However we have already seen that all homogeneous blends exhibited a 100% parallel behaviour, thus making it reasonable to assume this will also be the case for an individual phase of mixed composition within a heterogeneous blend.

One is left then with a one-parameter model for ternary blends

that allows for changes in composition within each phase. An example of the usefulness of such a model is shown in Figure 8. In this figure, data for E' and tan δ are presented for a ternary blend of composition 0.25/0.50/0.25 (COP 2148 (1/2)/BR/IR). By comparing these data with model predictions for different degrees of series-parallel coupling it was established that the behavior of this blend was 75% parallel. (The continuity of the BR phase in this blend had already been determined by thermal analysis (8,10) and electron microscopy (6,8,9) experiments). The continuous lines in Figure 8 correspond to the case for which all of the diblock, COP 2148 (1/2), goes to the IR phase; the dashed lines correspond to the case when all diblock goes to the BR phase. Note that in the rubbery region the effect of the location of the diblock is negligible. At lower temperatures, however, the shape and position of the transitions are better reproduced by assuming that all COP 2148 (1/2) goes to the IR, in agreement with the conclusions of earlier publications (6,8,9).

Various other binary and ternary blends containing 25% diblock were modelled following a procedure similar to the one outlined above. In each case the location of the diblock and the degree of series-parallel behavior were determined. Results are summarized in Table 3. These results also show that the percentage of parallel coupling increases as the amount of IR in the blend increases. Of even more significance is the agreement regarding the location of the diblock in these blends as ascertained from the present modelling study and as determined earlier from experiments (6,8,9). In ternary blends both COP 2144 (2/1) and COP 2148 (1/2) appear to reside mainly in the phase which is compatible with the longer segment of the diblock. COP 2143

(1/1), on the other hand, goes to the continuous phase.

TABLE 1

BR and IR Properties Used in Model for Homogeneous Blends

	IR	BR
T_g (^oK)	200	172
α_f($^oK^{-1} \times 10^{-4}$)	4.8	6.4
f_g	0.026	0.026

TABLE 2

Modelling of Homopolymer Blends

Blend Composition COP/BR/IR	% Parallel	Continuous Phase
0/0.75/0.25	0	BR
0/0.50/0.50	74	BR
0/0.25/0.75	90	IR

TABLE 3

Modelling of Blends Containing 25 wt % Diblock

Composition COP/BR/IR	% Parallel	Continuous Phase	Diblock Location
COP 2144 (2/1)			
0.25/0.75/0.0	---------- ONE PHASE BLEND ----------		
0.25/0.50/0.25	97	BR	BR
0.25/0.25/0.50	100	IR	BR
0.25/0.0/0.75	100	IR	*
COP 2143 (1/1)			
0.25/0.75/0.0	---------- ONE PHASE BLEND ----------		
0.25/0.50/0.25	0	BR	BR
0.25/0.25/0.50	100	IR	IR
0.25/0.0/0.75	---------- ONE PHASE BLEND ----------		
COP 2148 (1/2)			
0.25/0.75/0.0	0	BR	*
0.25/0.50/0.25	75	BR	IR
0.25/0.25/0.50	100	IR	IR
0.25/0.0/0.75	---------- ONE PHASE BLEND ----------		

*Diblock forms a separate phase in these blends.

Appendix

Temperature-Composition Shift

It may be assumed (14) that above the glass transition temperature T_g, the fraction of free volume f in a polymer i increases linearly with temperature in accordance with the relation:

$$f_i = f_{gi} + \alpha_{fi} (T - T_{gi}) \qquad (A1)$$

where f_{gi} is the free volume fraction at T_{gi} and α_{fi} is the thermal expansion of free volume relative to total volume.

Assuming additivity of free volumes, the free volume of a homogeneous blend of I and B can be calculated as

$$f_c = v_I f_I + v_B f_B \qquad (A2)$$

where v_I and v_B are the volume fraction of components I and B, respectively. Equation (A2) can also be expressed in terms of the free volume fraction of components I and B at their respective glass transition temperatures by using Equation (A1) to give

$$f_c = v_I \left[f_{gI}+\alpha_{fI}(T-T_{gI})\right] + v_B \left[f_{gB}+\alpha_{fB}(T-T_{gB})\right] \qquad (A3)$$

In order to determine the temperature T_I at which the free volume fraction of pure polymer I is equal to that in the blend at T_c, Equations (A1) and (A3) are combined to give:

$$f_{gI}+\alpha_{fI}(T_I-T_{gI})=v_I\left[f_{gI}+\alpha_{fI}(T_c-T_{gI})\right]+v_B\left[f_{gB}+\alpha_{fB}(T_c-T_{gB})\right] \qquad (A4)$$

which can be solved for T_I to yield:

$$T_I = \frac{v_I[f_{gI}+\alpha_{fI}(T_c-T_{gI})]+v_B[f_{gB}+\alpha_{fB}(T_c-T_{gB})]}{\alpha_I} - \frac{f_{gI}}{\alpha_I} + T_{gI} \qquad (A5)$$

An equation for T_B can be obtained in the same way. Likewise the extension to multiple components easily follows.

Calculation of E', E" and tan δ using Takayanagi's Model

The Takayanagi model equation for a blend of components M and N (M continuous) is (2):

$$E_D^* = (1 - \lambda) E_M^* + \left(\frac{1 - \phi}{E_M^*} + \frac{\phi}{E_N^*} \right)^{-1} \qquad (A6)$$

where E_D^*, E_M^* and E_N^* are the complex moduli of the blend and the components. The complex moduli in Equation (A6) can be substituted by the E' and E" components according to

$$E^* = E' + i\, E" \qquad (A7)$$

Thus, Equation (A6) becomes

$$E_D' + i\,E_D'' = (1-\lambda)\,(E_M' + i\,E_M'') + \lambda\left(\frac{1-\phi}{E_M'+i\,E_M''} + \frac{\phi}{E_N'+i\,E_N''}\right) \qquad (A8)$$

Expressions for E_D' and E_D'' can be obtained by separating the real and the imaginary parts of the right hand side of Equation (A8). After some manipulation one obtains

$$E_D' = \frac{AC + BD}{C^2 + D^2} \qquad (A9)$$

and

$$E_D'' = \frac{BC - AD}{C^2 + D^2} \qquad (A10)$$

where

$$A = (1-\lambda)\,(E_M'^2 - E_M''^2) + \lambda(E_M'\,E_N' - E_M''\,E_N'') \qquad (A11)$$

$$B = 2\,(1-\lambda)\,E_M'\,E_M'' + \lambda\,(E_M'E_N'' + E_M''E_N') \qquad (A12)$$

$$C = [1-\lambda(1-\phi)]\,E_M' + \lambda(1-\phi)\,E_N' \qquad (A13)$$

$$D = [1-\lambda(1-\phi)]\,E_N'' + \lambda(1-\phi)\,E_N'' \qquad (A14)$$

Finally

$$\tan\delta_D = \frac{E_D''}{E_D'} = \frac{B\,C - A\,D}{A\,C + B\,D} \qquad (A15)$$

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FIGURE LEGENDS

(1) Schematic summary of the experimental results obtained on the ternary system: cis 1,4 polyisoprene, 1,4 polybutadiene and corresponding diblock copolymers. shaded regions represent compositions for which homogeneous materials were obtained. The three diblocks, represented schematically below each ternary composition diagram, had molar polybutadiene to polyisoprene ratios of 2:1, 1:1 and 1:2 respectively. See references 6-10 for details.

(2) The Takayanagi model

(3) Temperatures of corresponding free volume, T_I and T_B, as a function of the sample temperature T_C for the case of the diblock with equimolar composition, COP 2143 (1/1).

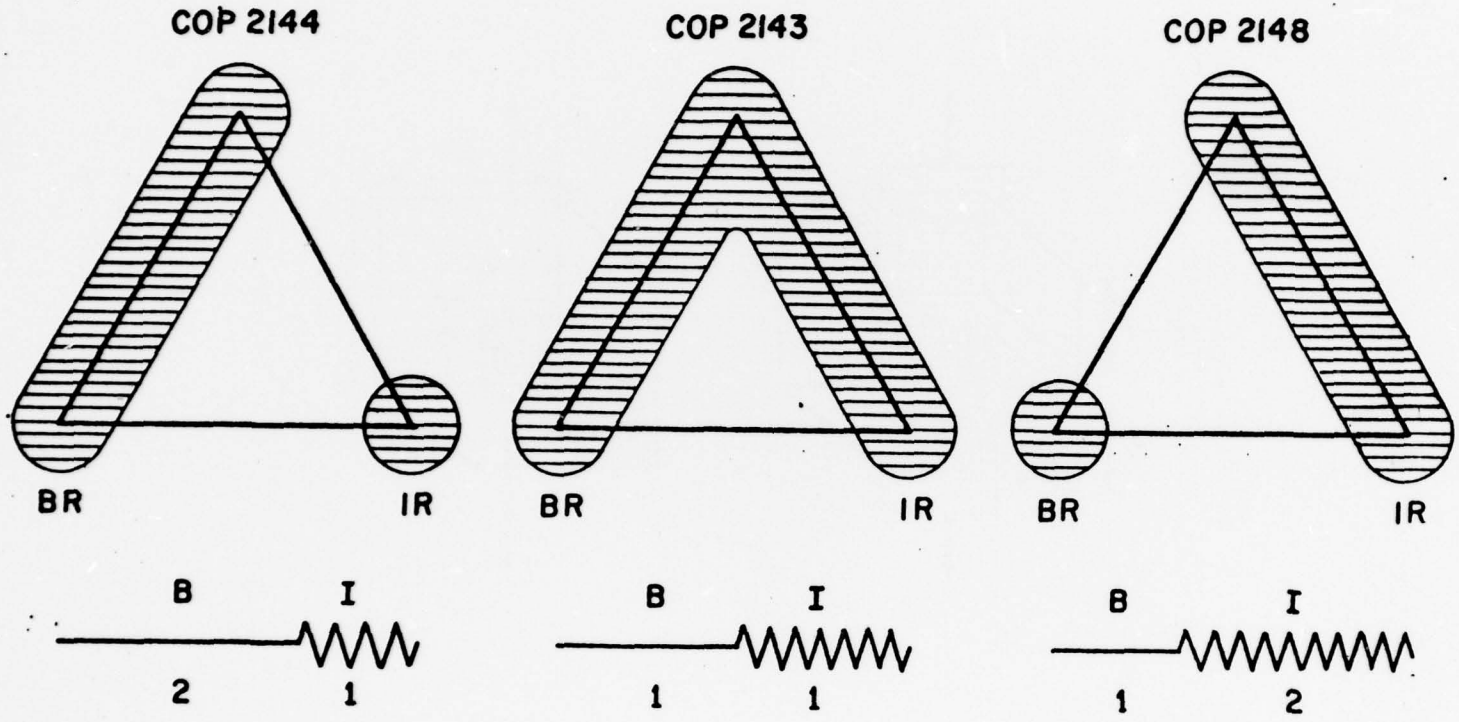
(4) Modelling of the viscoelastic behavior of homogeneous diblock COP 2143 (1/1).

(5) Modelling of the viscoelastic behavior of a homogeneous blend, 50 wt % diblock COP 2143 (1/1) and 50 wt % polyisoprene.

(6) Modelling of a heterogeneous blend, 50 wt % polybutadiene and 50 wt % polyisoprene, in which polybutadiene forms the continuous phase. The degree of parallel coupling is indicated on each curve.

(7) Modelling of a heterogeneous blend, 25 wt % polybutadiene and 75 wt % polyisoprene, in which polyisoprene forms the continuous phase. The degree of parallel coupling is indicated on each curve.

(8) Modelling of a ternary blend, 25 wt % COP 2148, 50 wt % polybutadiene, 25 wt % polyisoprene. Solid line is based on calculations which assume that the homogeneous diblock copolymer is solubilized completely by the polyisoprene. Dashed line - copolymer solubilized by the polybutadiene phase.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COP 2148
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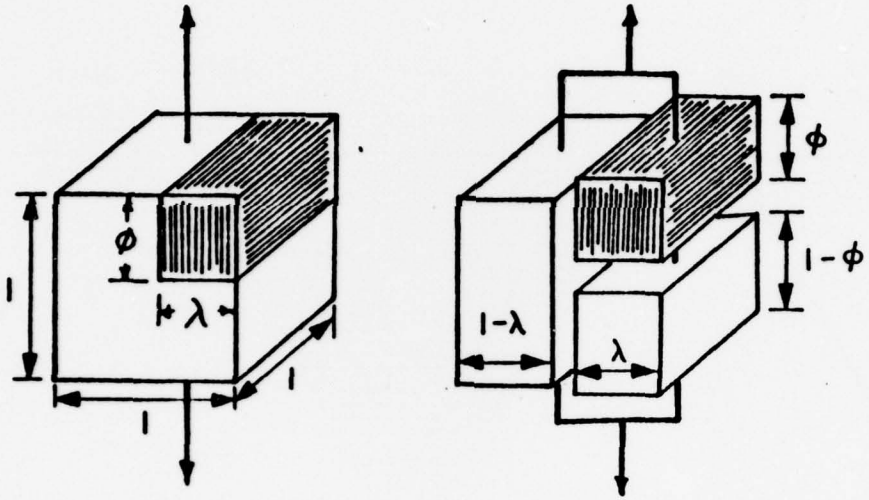
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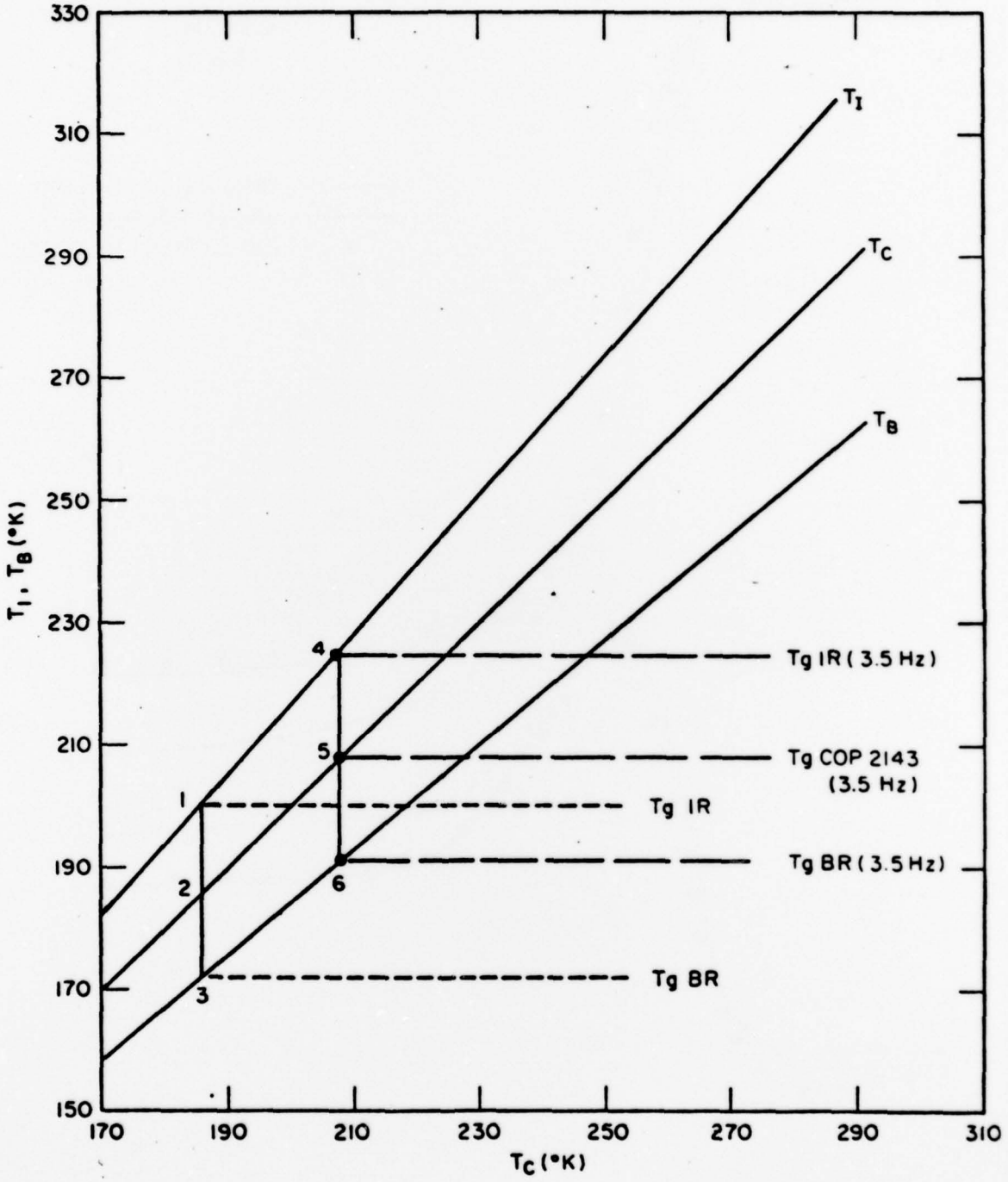
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310
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250
230
210
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170
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210
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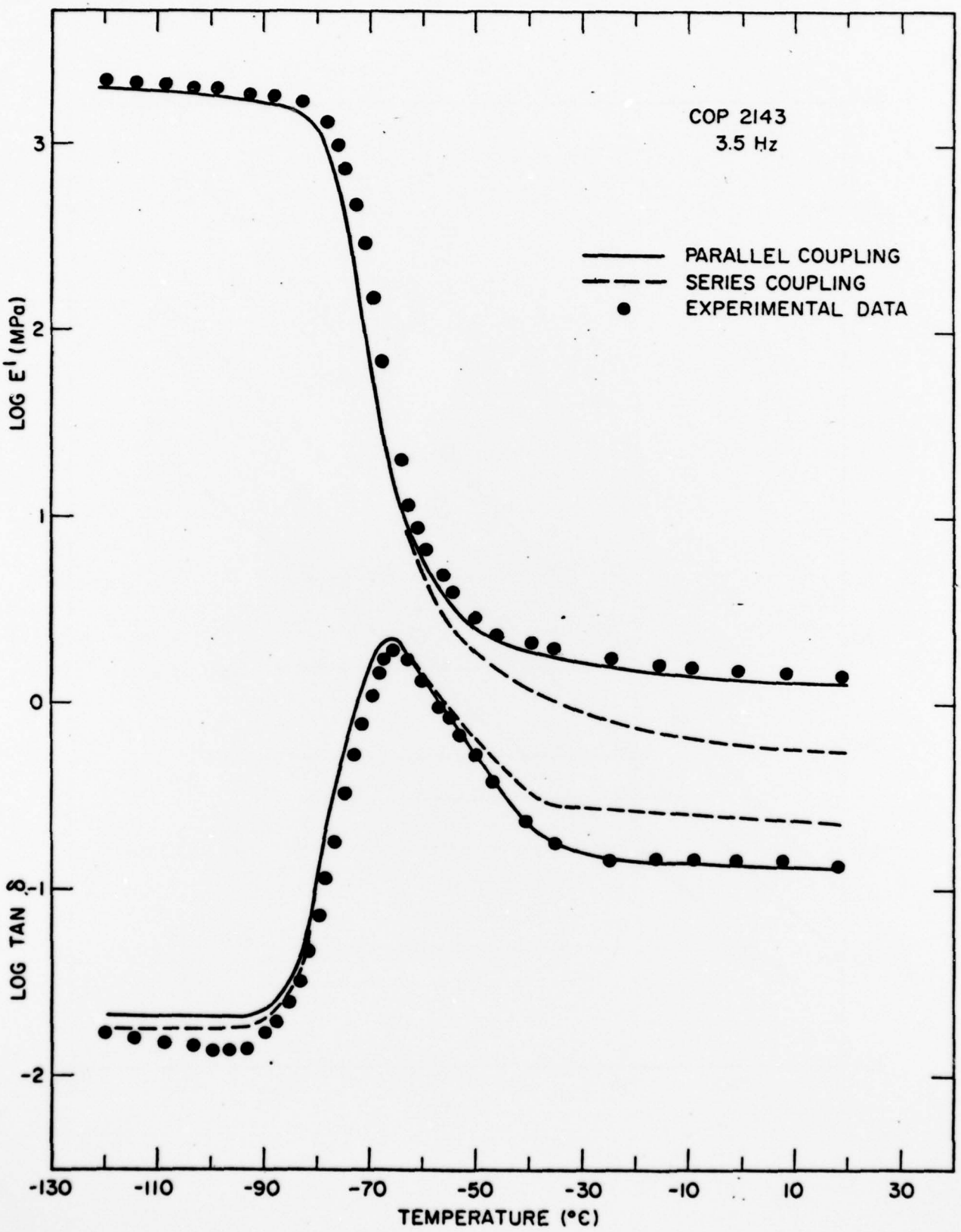
250
270
290
310
T_I
T_C
T_B
T_I, T_B (°K)
T_C (°K)
Tg IR (3.5 Hz)
Tg COP 2143
(3.5 Hz)
Tg IR
Tg BR (3.5 Hz)
Tg BR
1
2
3
4
5
6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3.5 Hz
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SERIES COUPLING
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LOG TAN δ
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1
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-1
-2
-130
-110
-90
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-30
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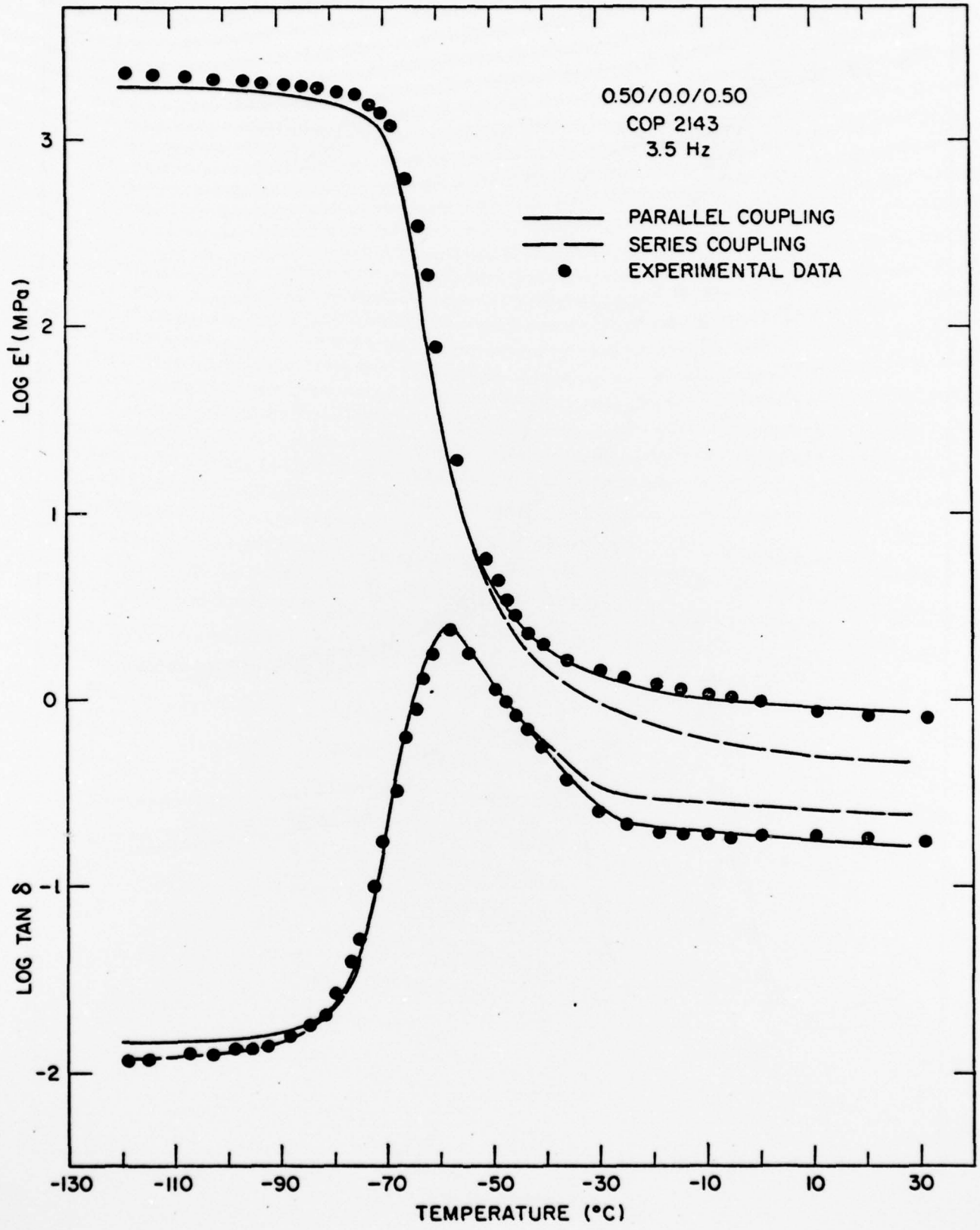
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3.5 Hz
PARALLEL COUPLING
SERIES COUPLING
EXPERIMENTAL DATA
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LOG TAN δ
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-1
-2
-130
-110
-90
-70
-50
-30
-10
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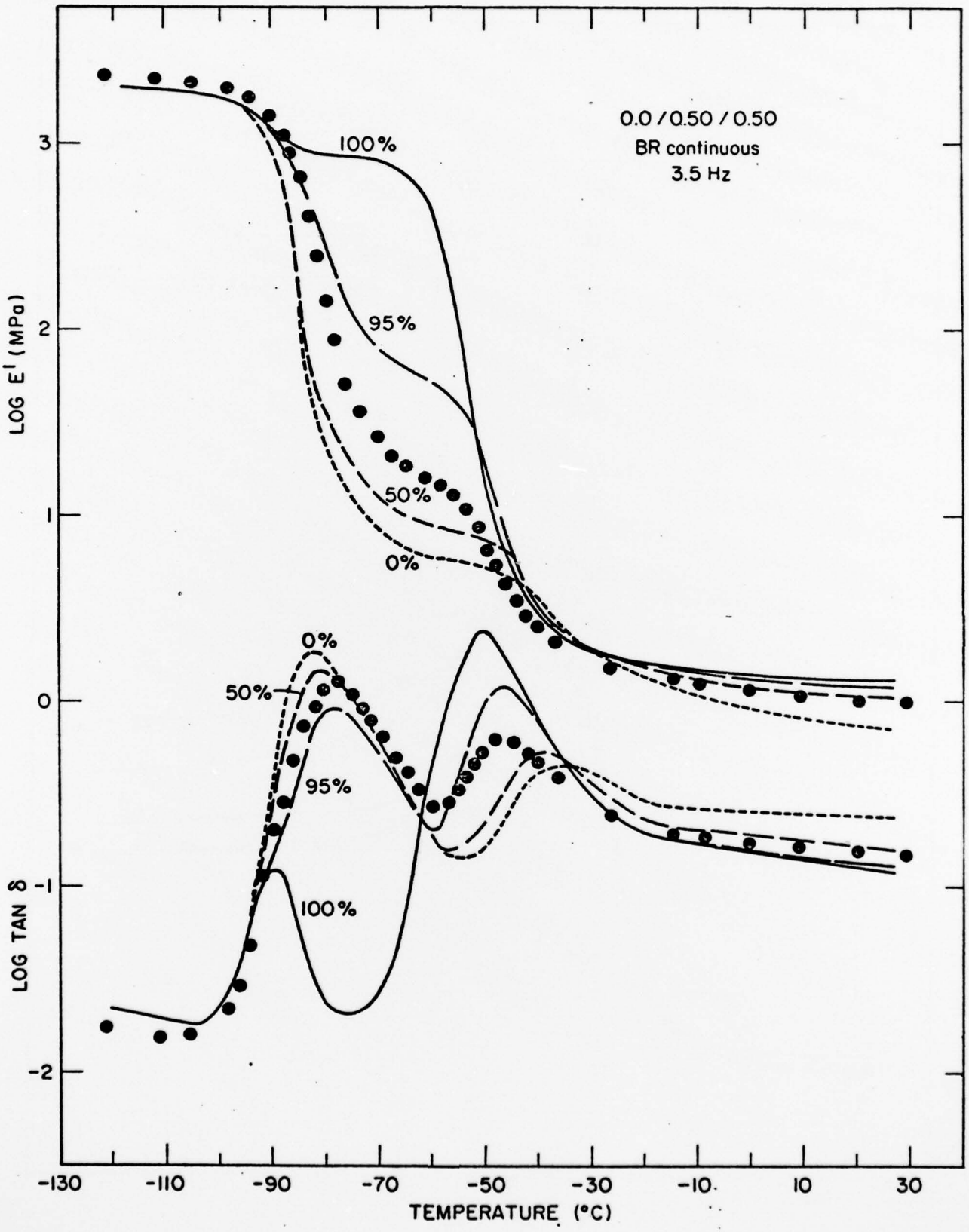
30
TEMPERATURE (°C)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BR continuous
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100%
95%
50%
0%
0%
50%
95%
100%
LOG E' (MPa)
LOG TAN δ
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0
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-2
-130
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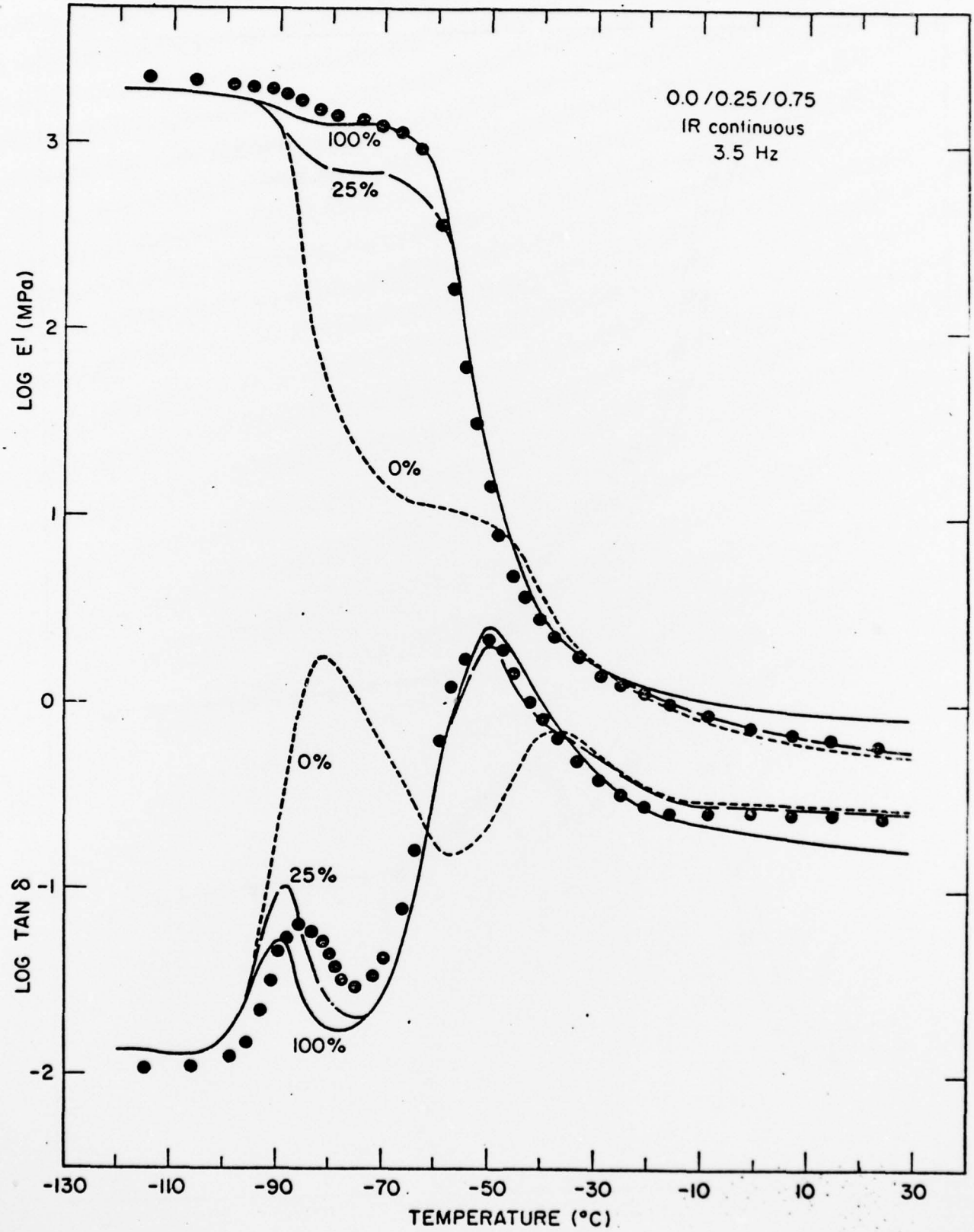
-90
-70
-50
-30
-10
10
30
TEMPERATURE (°C)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IR continuous
3.5 Hz
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LOG E' (MPa)
LOG TAN δ
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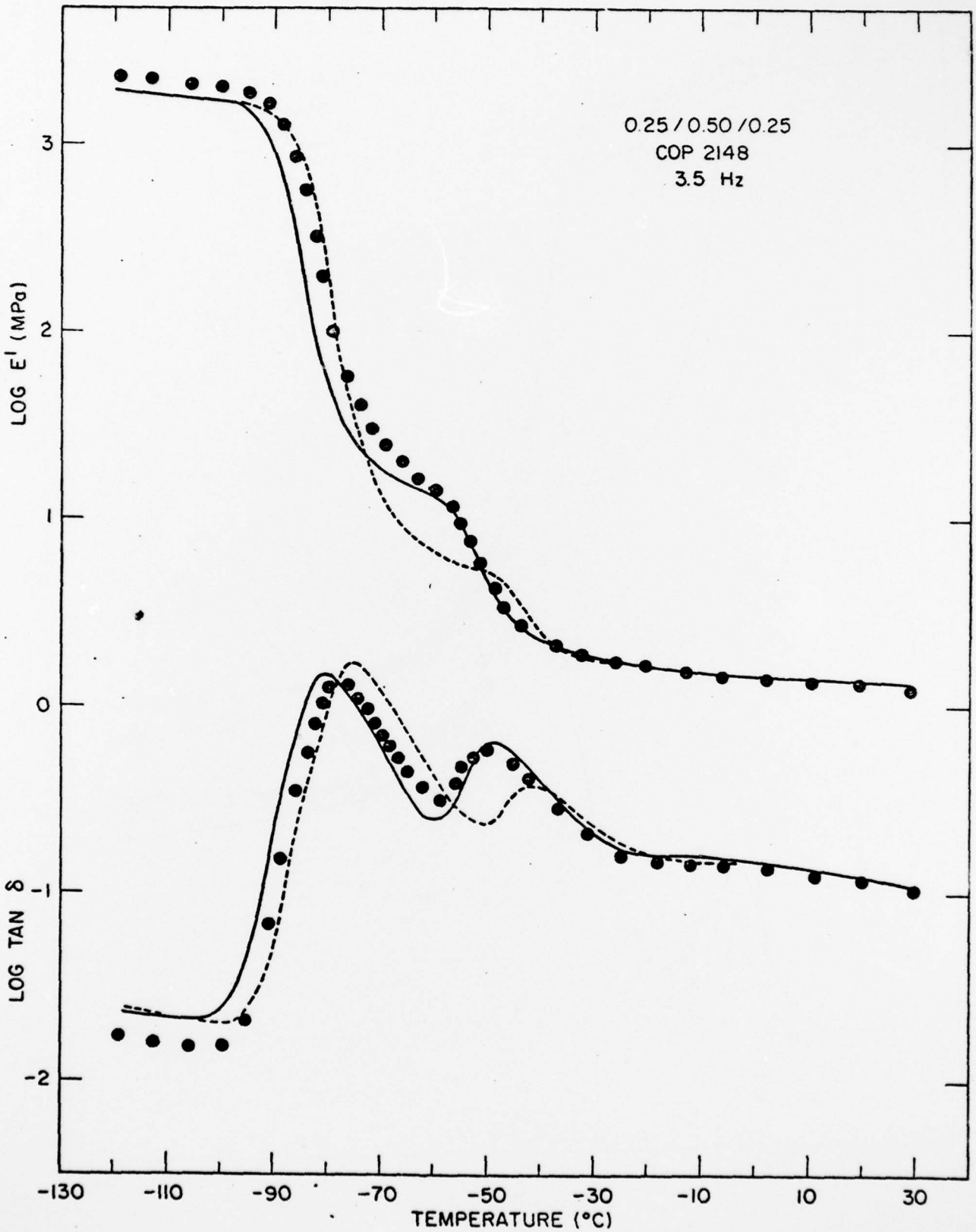
TEMPERATURE (°C)


0.25 / 0.50 / 0.25
COP 2148
3.5 Hz
LOG E' (MPa)
LOG TAN δ
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